(19)日本国特許庁（ＪＰ）　(12)公開特許公報（A）　(11)特許出願公開番号

特開平11－111267

(43)公開日　平成11年(1999)４月23日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｈ０１Ｍ　4/02		Ｈ０１Ｍ　4/02	Ｄ
4/04		4/04	Ａ
10/40		10/40	Ｚ
// Ｈ０１Ｍ　10/44		10/44	Ａ

審査請求　未請求　請求項の数１　ＯＬ　（全４頁）

(21)出願番号　特願平9－268405

(22)出願日　平成９年(1997)10月１日

(71)出願人　000003207
トヨタ自動車株式会社
愛知県豊田市トヨタ町１番地

(72)発明者　川本　浩二
愛知県豊田市トヨタ町１番地　トヨタ自動車株式会社内

(74)代理人　弁理士　吉田　研二　（外２名）

(54)【発明の名称】　リチウムイオン２次電池の製造方法

(57)【要約】

【課題】　負極表面に安定なＳＥＩを形成でき、不可逆容量を低減でき、サイクル特性の向上が図れる、リチウムイオン２次電池の製造方法を提供する。

【解決手段】　初回充電時の温度を２０℃以下とし、またその際の充電電流を１Ｃ以下とする条件のうち少なくともいずれか一方により初回充電を行い、負極表面に静電容量０．４ｍＦ／ｃｍ^{2}以下のＳＥＩ被膜を形成することを特徴とするリチウムイオン２次電池の製造方法である。

【特許請求の範囲】
【請求項1】　初回充電を、冷却雰囲気での充電及び1C以下の低電流充電のうちの少なくとも一方の条件で行い、負極表面に静電容量0．4mF／cm²以下のSEI被膜を形成することを特徴とするリチウムイオン2次電池の製造方法。
【発明の詳細な説明】
【0001】
【発明の属する技術分野】本発明は、リチウムイオン2次電池の製造方法の改良に関する。
【0002】
【従来の技術】リチウムイオン2次電池の負極表面には、通常SEI（Solid Electrolyte Interface）が形成されている。このSEIは、主として第1回目の充電時に負極表面に形成される。このSEIは、Li_2OやLi_2CO_3、LiF等のリチウム化合物であるため、ここに消費されたリチウムイオンは充電容量には寄与できず、初回充電時の不可逆容量すなわち充電容量と放電容量との差が増大することになる。この不可逆容量はSEIの形成量が多いほど大きくなる。このため、負極表面に形成されるSEIの量はなるべく少なくするのが望ましい。
【0003】図5には、20℃において充放電電流（1／3）Cの定電流で充放電を繰り返したときの充放電回数と不可逆容量との関係が示される。図5に示されるように、不可逆容量は1回目の充放電時が最も高くなっている。これは上述したように、1回目の充電時に負極表面に形成されるSEIの量が最も多いからである。
【0004】
【発明が解決しようとする課題】しかし、従来のリチウムイオン2次電池の製造方法においては、第1回目の充電を、室温（20～25℃）で行っている。また、初回の充電時間を短縮するために、充電電流も（1／3）C～1C程度で行われることが多い。ここで1Cは1時間率すなわち1時間で満充電とできる電流値を表し、（1／3）Cは1／3時間率すなわち1／3時間で満充電できる電流値を表している。このように、初回充電を常温でしかも1C以上の高い電流値で行った場合、負極表面に形成されるSEIの量が増えると共に、形成されるSEIがポーラスなものとなる。このため、2回目以降の充電時にもSEIが形成され、2回目以降の不可逆容量が増えるという問題があった。また、SEIの膜厚が厚くなり、負極の電気抵抗が増大するという問題もあった。さらに、常温でしかも高い電流値で充電した場合に負極表面に形成されるSEIでは、2次電池の放電中にそのSEI中のリチウムも放電し、SEIが分解されて安定なSEIを得ることができない。このため、充電の度にSEIが負極表面に形成され、サイクル特性が低下するという問題もあった。
【0005】本発明は、上記従来の課題に鑑みなされたものであり、その目的は、負極表面に安定なSEIを形成でき、不可逆容量を低減でき、サイクル特性の向上が図れる、リチウムイオン2次電池の製造方法を提供することにある。
【0006】
【課題を解決するための手段】上記目的を達成するために、本発明は、初回充電を、冷却雰囲気での充電及び1C以下の低電流充電のうちの少なくとも一方の条件で行い、負極表面に静電容量0．4mF／cm²以下のSEI被膜を形成することを特徴とする。
【0007】
【発明の実施の形態】以下、本発明の実施の形態（以下実施形態という）を、説明する。
【0008】本発明者らは、初回充電時に負極表面に形成されるSEIの量を減らすと共に、この時に生じるSEIを安定なものとし、2サイクル目以降に負極表面に形成されるSEIを減らすために検討を進めた。その結果、初回充電を、冷却された雰囲気すなわち低温で実施したり、あるいは1C以下の低電流で充電することが有効であることを見いだした。
【0009】上記検討に使用したリチウムイオン2次電池は以下のものである。天然黒鉛：PVDF＝9：1の混合物と、溶媒としてNMPを用い、これらによりペーストを作成した後このペーストを銅箔上に塗布乾燥し、8mg／cm²の負極電極を得た。この負極電極を、セパレータを介して対極であるリチウム箔と組み合わせた後、1mol／l－$LiBF_4$を含むPC：EC：DEC＝2：3：5の電解液に浸し、負極の充放電特性を調べた。
【0010】図1には、充電時の温度と不可逆容量との関係が示される。図1においては、充放電電流を（1／3）Cの一定電流とし、各温度毎に2サイクル充放電を行った後、更に20℃として3サイクル充放電させたときの不可逆容量の合計が縦軸に示されている。図1より、充電時の温度を低下させると、不可逆容量が低減できることがわかる。
【0011】図2には、充電電流の大きさと不可逆容量との関係が示される。図2においては、充電時の温度を20℃とし、始め2サイクルの充電電流を変化させ、その後3サイクルを（1／3）Cの一定電流で充放電させたときの不可逆容量の合計が縦軸に示されている。図2からわかるように、始め2サイクルの充電電流の値が低い方が不可逆容量が低減していることがわかる。図2の結果より、初回の充電電流としては、1C以下の低電流で充電するのが望ましいことがわかる。
【0012】次に、初回充電時の温度条件を更に詳細に検討した。図3には、初回充電の温度条件と負極に形成されたSEIの静電容量との関係が示される。負極表面に形成されるSEIが多いほどその静電容量も上昇するものと考えられる。この静電容量は、インピーダンス測

定を行い、コールーコールプロット法により求めた。

【0013】また、図4には、上述したＳＥＩの静電容量と不可逆容量との関係が示される。図4からわかるように、ＳＥＩによる静電容量が0．4ｍＦ／ｃｍ²以下の場合に不可逆容量が大きく低下することがわかる。この0．4ｍＦ／ｃｍ²の静電容量は、初回充電時の温度を２０℃とした場合に生じるＳＥＩの静電容量であることが図3からわかる。以上より、初回充電は、２０℃以下の冷却雰囲気で行うのが望ましい。

【0014】初回充電を低温で行う場合の効果を確認するために、－２０℃の温度で充電電流を（１／３）Ｃとし、放電電流も（１／３）Ｃとして2サイクル充放電を行った。この後更に２０℃で（１／３）Ｃの充放電を3サイクル行った場合の不可逆容量は４２ｍＡｈ／ｇとなり、不可逆容量の低下が確認された。また、負極表面に形成されるＳＥＩの安定性を調べるために、初期充電を２０℃、（１／３）Ｃの充電電流で行ったリチウムイオン2次電池と、－２０℃、（１／３）Ｃの充電電流で2サイクル充放電を行った後２０℃の温度において（１／３）Ｃの充放電電流で3サイクル充放電を行わせた本発明の製造方法に係るリチウムイオン2次電池とを使用し、これら2種類のリチウムイオン2次電池を５日間放電状態で放置した。この後、再度２０℃で（１／３）Ｃの充放電を行い、3サイクル合計の不可逆容量を測定した。この結果上記２０℃の温度で（１／３）Ｃの充電電流で初回充電を行った従来例では、不可逆容量が１６ｍＡｈ／ｇであったのに対し、本発明に係る製造方法によって製造したものについては８ｍＡｈ／ｇとなった。このように、本発明に係る製造方法により製造したリチウムイオン2次電池の方が不可逆容量が低下するのは、安定したＳＥＩが生成しているためと考えられ、サイクル特性の向上が図れることがわかった。

【0015】以上の通り、リチウムイオン2次電池を製造する際には、２０℃以下の冷却雰囲気、あるいは１Ｃ以下の低電流で初回の充電を行うことが負極表面に形成されるＳＥＩの量の低減と生じるＳＥＩの安定化に有効であることを見いだせた。

【0016】

【発明の効果】以上説明したように、本発明によれば、負極表面に形成されるＳＥＩの量が低減し、不可逆容量を減少させることができるとともに、生じるＳＥＩが安定しているため、サイクル特性の向上も図ることができる。

【図面の簡単な説明】

【図1】　初回充電時の温度と不可逆容量との関係を示す図である。

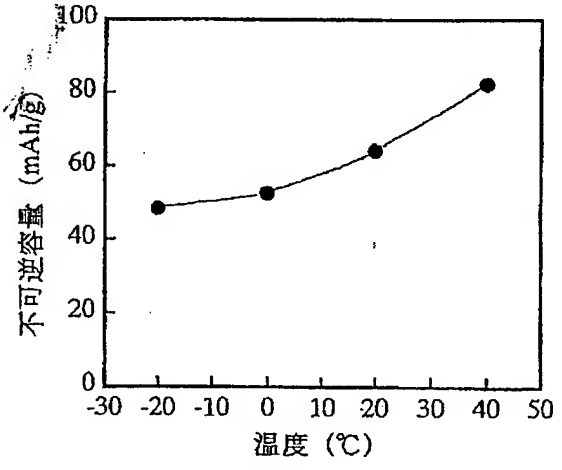
【図2】　初回充電時の充電電流と不可逆容量との関係を示す図である。

【図3】　初回充電時の温度と、その際に発生するＳＥＩの静電容量との関係を示す図である。

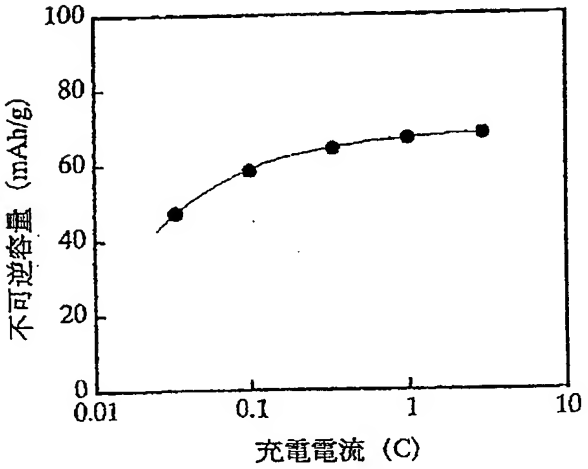
【図4】　ＳＥＩの静電容量と不可逆容量との関係を示す図である。

【図5】　リチウムイオン2次電池における充放電回数と不可逆容量との関係を示す図である。

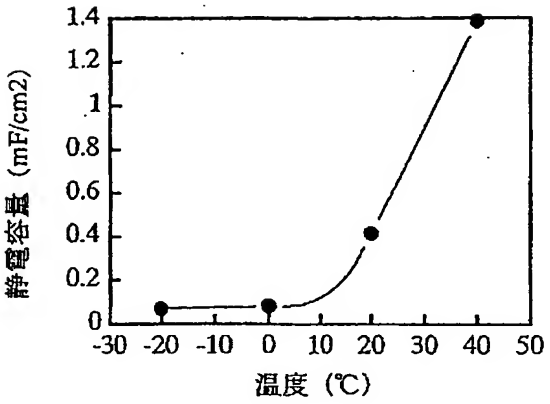
【図1】



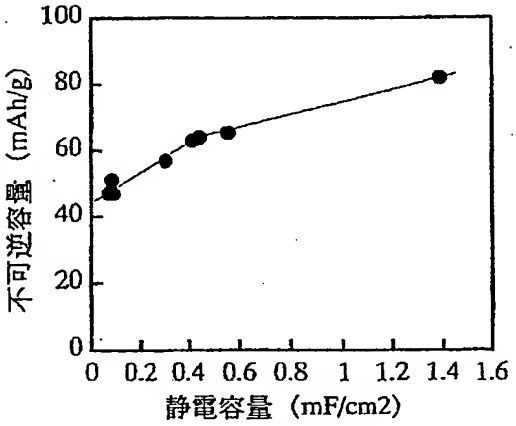
【図2】



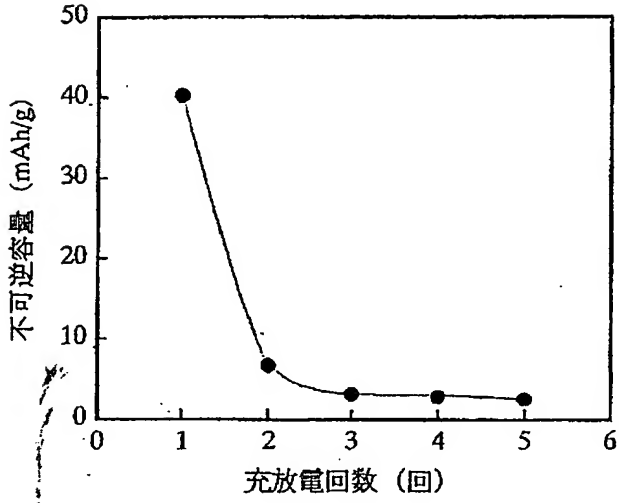
【図3】


静電容量（mF/cm2）
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-30 -20 -10 0 10 20 30 40 50
温度（℃）

【図4】


不可逆容量（mAh/g）
100
80
60
40
20
0
0 0.2 0.4 0.6 0.8 1 1.2 1.4 1.6
静電容量（mF/cm2）

【図5】


不可逆容量（mAh/g）
50
40
30
20
10
0
0 1 2 3 4 5 6
充放電回数（回）

PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-111267**
(43)Date of publication of application : **23.04.1999**

(51)Int.CI. H01M 4/02
H01M 4/04
H01M 10/40
// H01M 10/44

(21)Application number : **09-268405**
(22)Date of filing : **01.10.1997**

(71)Applicant : **TOYOTA MOTOR CORP**
(72)Inventor : **KAWAMOTO KOJI**

(54) MANUFACTURE OF LITHIUM TON SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To form a stable SET on a negative electrode surface, reduce irreversible capacity, and improve a cycle characteristic by performing first time charge at least under one condition among charge in a cooling atmosphere and low electric current charge, and forming an SEI coating film having specific capacitance on the negative electrode surface.
SOLUTION: When a charging time temperature is lowered from the relationship between the charging time temperature and irreversible capacity, the irreversible capacity can be reduced. Therefore, it is effective to perform first time charge in a cooling atmosphere, that is, at a low temperature not more than 20°C or perform charge by a low electric current not more than 1 C. The irreversible capacity sharply reduces when capacitance by an SET is not more than 0.4 mF/cm2 from the relationship between the capacitance of the SET and the irreversible capacity. Then, an SEI coating film having capacitance not more than 0.4 mF/cm2 is formed on a nagative electrode surface, a quantity of the SET formed on the negative electrode surface reduces, and the irreversible capacity is reduced, and since the generating SET is stable, a cycle characteristic can also be improved.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the lithium ion rechargeable battery characterized by performing first time charge on condition that either [at least] charge in cooling atmosphere, or the low-current charge below 1C, and forming a two or less electrostatic-capacity 0.4 mF/cm SEI coat in a negative-electrode front face.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to improvement of the manufacture method of a lithium ion rechargeable battery.
[0002]
[Description of the Prior Art] SEI (Solid Electrolyte Interface) is usually formed in the negative-electrode front face of a lithium ion rechargeable battery. This SEI is formed in a negative-electrode front face mainly at the time of the 1st charge. this SEI -- Li2O and Li2 -- since it is lithium compounds, such as CO3 and LiF, the lithium ion consumed here cannot be contributed to charge capacity, but a difference with the irreversible capacity at the time of first time charge, i.e., charge capacity, and service capacity will increase This irreversible capacity becomes so large that there are many amounts of formation of SEI. For this reason, as for the amount of SEI formed in a negative-electrode front face, lessening if possible is desirable.
[0003] The relation between the number of times of charge and discharge when repeating charge and discharge in 20 degrees C by the constant current of a charge and discharge current (1/3) C and irreversible capacity is shown in drawing 5 . As shown in drawing 5 , it has become high [the time of the 1st charge and discharge] most [irreversible capacity]. This is because there are most amounts of SEI formed in a negative-electrode front face at the time of the 1st charge as mentioned above.
[0004]
[Problem(s) to be Solved by the Invention] However, in the manufacture method of the conventional lithium ion rechargeable battery, 1st charge is performed at the room temperature (20-25 degrees C). Moreover, in order to shorten the first-time charging time, the charging current is also performed in many cases by about C(1/3) -1C. 1C expresses the made current value as a full charge in 1 hour rate, i.e., 1 hour, here, and C (1/3) expresses the current value which can carry out a full charge in 1/3 hour rate, i.e., 3 hours in 1/hours. Thus, SEI formed will become porous, while the amount of SEI formed in a negative-electrode front face increases, when the high current value more than 1C moreover performs first time charge in ordinary temperature. For this reason, SEI was formed also at the time of charge of the 2nd henceforth, and there was a problem that the irreversible capacity of the 2nd henceforth increased. Moreover, the thickness of SEI became thick and the problem that the electric resistance of a negative electrode increased also had it. Furthermore, in SEI formed in a negative-electrode front face when it moreover charges by high current value in ordinary temperature, the lithium in the SEI also discharges during electric discharge of a rechargeable battery, SEI is decomposed, and stable SEI cannot be obtained. For this reason, SEI was formed in the negative-electrode front face at the degree of charge, and there was also a problem that a cycle property fell.
[0005] this invention is made in view of the above-mentioned conventional technical problem, and the purpose is in offering the manufacture method of the lithium ion rechargeable battery which can form stable SEI in a negative-electrode front face, can reduce irreversible capacity, and can aim at improvement in a cycle property.

[0006]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention performs first time charge on condition that either [at least] charge in cooling atmosphere, or the low-current charge below 1C, and is characterized by forming a two or less electrostatic-capacity 0.4 mF/cm SEI coat in a negative-electrode front face.
[0007]
[Embodiments of the Invention] Hereafter, the gestalt (henceforth an operation gestalt) of operation of this invention is explained.
[0008] This invention persons made stable SEI produced at this time, and in order to reduce SEI formed in a negative-electrode front face after a two-cycle eye, they advanced examination, while they reduced the amount of SEI formed in a negative-electrode front face at the time of first time charge. Consequently, first time charge was carried out, the cooled atmosphere, i.e., the low temperature, or it found out that it was effective to charge by the low current below 1C.
[0009] The lithium ion rechargeable batteries used for the above-mentioned examination are as follows. Natural graphite :P Using NMP as the mixture of VDF=9:1, and a solvent, after creating a paste by these, application dryness of this paste was carried out on copper foil, and the negative-electrode electrode of 8 mg/cm2 was obtained. After combining this negative-electrode electrode with the lithium foil which is a counter electrode through separator, it dipped in the electrolytic solution of PC:EC:DEC=2:3:5 containing 1 mol/l-LiBF4, and the charge-and-discharge property of a negative electrode was investigated.
[0010] The relation between the temperature at the time of charge and irreversible capacity is shown in drawing 1 . In drawing 1 , after making a charge and discharge current into the fixed current of C (1/3) and performing two-cycle charge and discharge for every temperature, the sum total of the irreversible capacity when carrying out 3 cycle charge and discharge as 20 more degrees C is shown in the vertical axis. Drawing 1 shows that irreversible capacity can be reduced, when the temperature at the time of charge is reduced.
[0011] The relation between the size of the charging current and irreversible capacity is shown in drawing 2 . In drawing 2 , temperature at the time of charge is made into 20 degrees C, and is begun, the charging current of a two cycle is changed, and the sum total of the irreversible capacity when carrying out the charge and discharge of the 3 cycle with the fixed current of C (1/3) after that is shown in the vertical axis. As drawing 2 shows, it turns out that it begins and irreversible capacity is decreasing [the value of the charging current of a two cycle / the method of a low]. It turns out that it is more desirable than the result of drawing 2 as the first-time charging current to charge by the low current below 1C.
[0012] Next, the temperature conditions at the time of first time charge were examined still in detail. The relation between the temperature conditions of first time charge and the electrostatic capacity of SEI formed in the negative electrode is shown in drawing 3 . It is thought that the electrostatic capacity also rises, so that there are many SEIs formed in a negative-electrode front face. This electrostatic capacity performed impedance measurement and asked for it by the Cole-Cole-plot method.
[0013] Moreover, the relation of the electrostatic capacity of SEI and irreversible capacity which were mentioned above is shown in drawing 4 . When the electrostatic capacity by SEI is two or less 0.4 mF/cm so that drawing 4 may show, it turns out that irreversible capacity falls greatly. Drawing 3 shows that it is the electrostatic capacity of SEI produced when the electrostatic capacity of these 0.4 mF/cm2 makes temperature at the time of first time charge 20 degrees C. As mentioned above, it is desirable to perform first time charge in cooling atmosphere 20 degrees C or less.
[0014] in order to check the effect in the case of performing first time charge at low temperature, the charging current was set to C (1/3) at the temperature which is -20 degrees C, and the discharge current also performed two-cycle charge and discharge as C (1/3) The irreversible capacity of 3 cycle ****** case became 42 mAh/g about the charge and discharge of C (1/3) at 20 more degrees C after this, and the fall of irreversible capacity was checked. Moreover, the lithium ion rechargeable battery which performed initial charge by the charging current of 20 degrees C and C (1/3) in order to investigate the stability of SEI formed in a negative-electrode front face, - Use Lithium Ion Rechargeable Battery

Concerning the Manufacture Method of this Invention of Having Made 3 Cycle Charge and Discharge Performing by Charge and Discharge Current of C (1/3) in Temperature of 20 Degrees C after Performing Two-Cycle Charge and Discharge by Charging Current of 20 Degrees C and C (1/3). These two kinds of lithium ion rechargeable batteries were left in the state of electric discharge for five days. Then, the charge and discharge of C (1/3) were again performed at 20 degrees C, and the irreversible capacity of 3 cycle sum total was measured. About what was manufactured by the manufacture method which starts this invention to irreversible capacity having been 16 mAh/g in the conventional example which performed first time charge by the charging current of C (1/3) with the temperature of the above-mentioned 20 degrees C as a result, it became 8 mAh/g. Thus, it turns out that it thinks because SEI in which the direction of the lithium ion rechargeable battery manufactured by the manufacture method concerning this invention was stabilized by that irreversible capacity falls is generating, and improvement in a cycle property can be aimed at.

[0015] When manufacturing a lithium ion rechargeable battery as above, charging the first time by the low current below cooling atmosphere 20 degrees C or less or 1C was able to find out that it was effective in reduction of the amount of SEI formed in a negative-electrode front face, and stabilization of SEI to produce.

[0016]

[Effect of the Invention] Since SEI to produce is stable while according to this invention the amount of SEI formed in a negative-electrode front face can decrease and being able to decrease irreversible capacity, as explained above, improvement in a cycle property can also be aimed at.

[Translation done.]

* NOTICES *

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to improvement of the manufacture method of a lithium ion rechargeable battery.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] SEI (Solid Electrolyte Interface) is usually formed in the negative-electrode front face of a lithium ion rechargeable battery. This SEI is formed in a negative-electrode front face mainly at the time of the 1st charge. this SEI -- Li2O and Li2 -- since it is lithium compounds, such as CO3 and LiF, the lithium ion consumed here cannot be contributed to charge capacity, but a difference with the irreversible capacity at the time of first time charge, i.e., charge capacity, and service capacity will increase This irreversible capacity becomes so large that there are many amounts of formation of SEI. For this reason, as for the amount of SEI formed in a negative-electrode front face, lessening if possible is desirable.
[0003] The relation between the number of times of charge and discharge when repeating charge and discharge in 20 degrees C by the constant current of a charge and discharge current (1/3) C and irreversible capacity is shown in drawing 5 . As shown in drawing 5 , it has become high [the time of the 1st charge and discharge] most [irreversible capacity]. This is because there are most amounts of SEI formed in a negative-electrode front face at the time of the 1st charge as mentioned above.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] Since SEI to produce is stable while according to this invention the amount of SEI formed in a negative-electrode front face can decrease and being able to decrease irreversible capacity, as explained above, improvement in a cycle property can also be aimed at.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, in the manufacture method of the conventional lithium ion rechargeable battery, 1st charge is performed at the room temperature (20-25 degrees C). Moreover, in order to shorten the first-time charging time, the charging current is also performed in many cases by about C(1/3) -1C. 1C expresses the made current value as a full charge in 1 hour rate, i.e., 1 hour, here, and C (1/3) expresses the current value which can carry out a full charge in 1/3 hour rate, i.e., 3 hours in 1/hours. Thus, SEI formed will become porous, while the amount of SEI formed in a negative-electrode front face increases, when the high current value more than 1C moreover performs first time charge in ordinary temperature. For this reason, SEI was formed also at the time of charge of the 2nd henceforth, and there was a problem that the irreversible capacity of the 2nd henceforth increased. Moreover, the thickness of SEI became thick and the problem that the electric resistance of a negative electrode increased also had it. Furthermore, in SEI formed in a negative-electrode front face when it moreover charges by high current value in ordinary temperature, the lithium in the SEI also discharges during electric discharge of a rechargeable battery, SEI is decomposed, and stable SEI cannot be obtained. For this reason, SEI was formed in the negative-electrode front face at the degree of charge, and there was also a problem that a cycle property fell.
[0005] this invention is made in view of the above-mentioned conventional technical problem, and the purpose is in offering the manufacture method of the lithium ion rechargeable battery which can form stable SEI in a negative-electrode front face, can reduce irreversible capacity, and can aim at improvement in a cycle property.

[Translation done.]

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention performs first time charge on condition that either [at least] charge in cooling atmosphere, or the low-current charge below 1C, and is characterized by forming a two or less electrostatic-capacity 0.4 mF/cm SEI coat in a negative-electrode front face.
[0007]
[Embodiments of the Invention] Hereafter, the gestalt (henceforth an operation gestalt) of operation of this invention is explained.
[0008] This invention persons made stable SEI produced at this time, and in order to reduce SEI formed in a negative-electrode front face after a two-cycle eye, they advanced examination, while they reduced the amount of SEI formed in a negative-electrode front face at the time of first time charge. Consequently, first time charge was carried out, the cooled atmosphere, i.e., the low temperature, or it found out that it was effective to charge by the low current below 1C.
[0009] The lithium ion rechargeable batteries used for the above-mentioned examination are as follows. Natural graphite :P Using NMP as the mixture of VDF=9:1, and a solvent, after creating a paste by these, application dryness of this paste was carried out on copper foil, and the negative-electrode electrode of 8 mg/cm2 was obtained. After combining this negative-electrode electrode with the lithium foil which is a counter electrode through separator, it dipped in the electrolytic solution of PC:EC:DEC=2:3:5 containing 1 mol/l-LiBF4, and the charge-and-discharge property of a negative electrode was investigated.
[0010] The relation between the temperature at the time of charge and irreversible capacity is shown in drawing 1 . In drawing 1 , after making a charge and discharge current into the fixed current of C (1/3) and performing two-cycle charge and discharge for every temperature, the sum total of the irreversible capacity when carrying out 3 cycle charge and discharge as 20 more degrees C is shown in the vertical axis. Drawing 1 shows that irreversible capacity can be reduced, when the temperature at the time of charge is reduced.
[0011] The relation between the size of the charging current and irreversible capacity is shown in drawing 2 . In drawing 2 , temperature at the time of charge is made into 20 degrees C, and is begun, the charging current of a two cycle is changed, and the sum total of the irreversible capacity when carrying out the charge and discharge of the 3 cycle with the fixed current of C (1/3) after that is shown in the vertical axis. As drawing 2 shows, it turns out that it begins and irreversible capacity is decreasing [the value of the charging current of a two cycle / the method of a low]. It turns out that it is more desirable than the result of drawing 2 as the first-time charging current to charge by the low current below 1C.
[0012] Next, the temperature conditions at the time of first time charge were examined still in detail. The relation between the temperature conditions of first time charge and the electrostatic capacity of SEI formed in the negative electrode is shown in drawing 3 . It is thought that the electrostatic capacity also rises, so that there are many SEIs formed in a negative-electrode front face. This electrostatic capacity performed impedance measurement and asked for it by the Cole-Cole-plot method.
[0013] Moreover, the relation of the electrostatic capacity of SEI and irreversible capacity which were

mentioned above is shown in drawing 4 . When the electrostatic capacity by SEI is two or less 0.4 mF/cm so that drawing 4 may show, it turns out that irreversible capacity falls greatly. Drawing 3 shows that it is the electrostatic capacity of SEI produced when the electrostatic capacity of these 0.4 mF/cm2 makes temperature at the time of first time charge 20 degrees C. As mentioned above, it is desirable to perform first time charge in cooling atmosphere 20 degrees C or less.

[0014] in order to check the effect in the case of performing first time charge at low temperature, the charging current was set to C (1/3) at the temperature which is -20 degrees C, and the discharge current also performed two-cycle charge and discharge as C (1/3) The irreversible capacity of 3 cycle ****** case became 42 mAh/g about the charge and discharge of C (1/3) at 20 more degrees C after this, and the fall of irreversible capacity was checked. Moreover, the lithium ion rechargeable battery which performed initial charge by the charging current of 20 degrees C and C (1/3) in order to investigate the stability of SEI formed in a negative-electrode front face, - Use Lithium Ion Rechargeable Battery Concerning the Manufacture Method of this Invention of Having Made 3 Cycle Charge and Discharge Performing by Charge and Discharge Current of C (1/3) in Temperature of 20 Degrees C after Performing Two-Cycle Charge and Discharge by Charging Current of 20 Degrees C and C (1/3). These two kinds of lithium ion rechargeable batteries were left in the state of electric discharge for five days. Then, the charge and discharge of C (1/3) were again performed at 20 degrees C, and the irreversible capacity of 3 cycle sum total was measured. About what was manufactured by the manufacture method which starts this invention to irreversible capacity having been 16 mAh/g in the conventional example which performed first time charge by the charging current of C (1/3) with the temperature of the above-mentioned 20 degrees C as a result, it became 8 mAh/g. Thus, it turns out that it thinks because SEI in which the direction of the lithium ion rechargeable battery manufactured by the manufacture method concerning this invention was stabilized by that irreversible capacity falls is generating, and improvement in a cycle property can be aimed at.

[0015] When manufacturing a lithium ion rechargeable battery as above, charging the first time by the low current below cooling atmosphere 20 degrees C or less or 1C was able to find out that it was effective in reduction of the amount of SEI formed in a negative-electrode front face, and stabilization of SEI to produce.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the relation between the temperature at the time of first time charge, and irreversible capacity.
[Drawing 2] It is drawing showing the relation between the charging current at the time of first time charge, and irreversible capacity.
[Drawing 3] It is drawing showing the relation between the temperature at the time of first time charge, and the electrostatic capacity of SEI generated in that case.
[Drawing 4] It is drawing showing the relation between the electrostatic capacity of SEI, and irreversible capacity.
[Drawing 5] It is drawing showing the relation of the number of times of charge and discharge and irreversible capacity in a lithium ion rechargeable battery.

[Translation done.]

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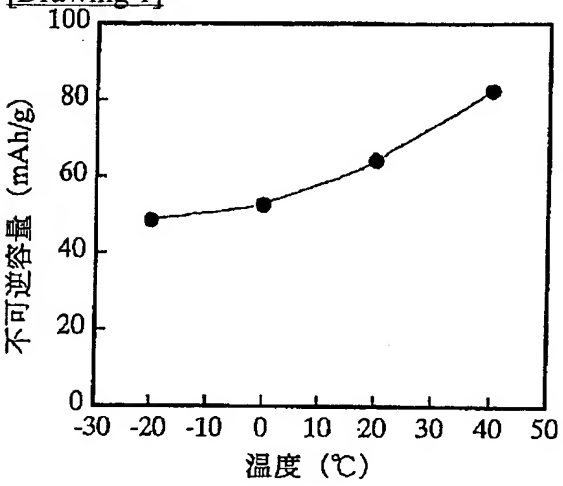
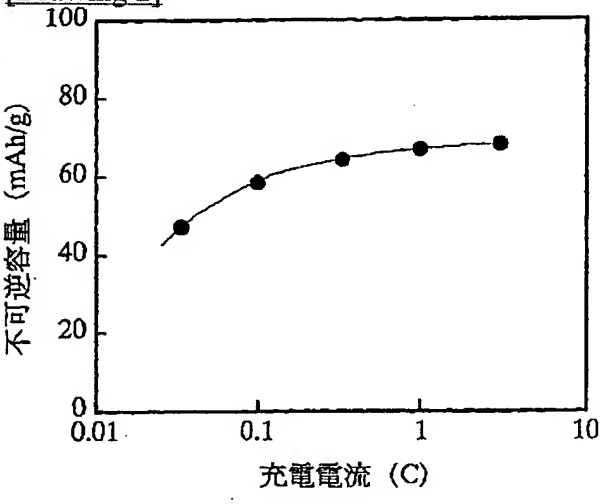
DRAWINGS

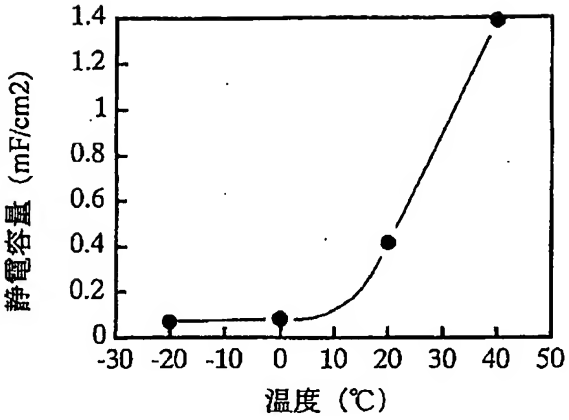
[Drawing 1]



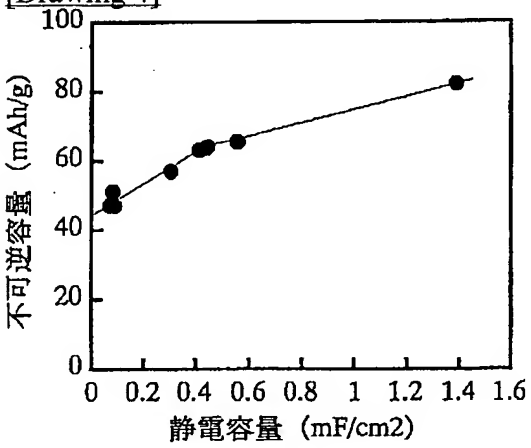
[Drawing 2]



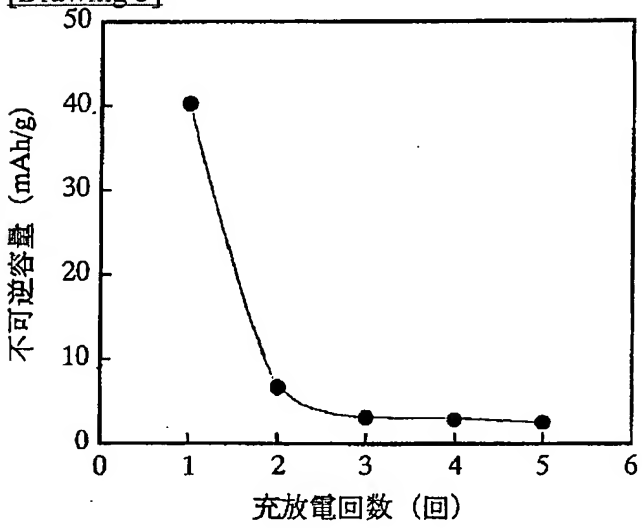
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]